RESONANT SOFT X-RAY EMISSION SPECTROSCOPY OF V_2O_3, VO_2 and NaV_2O_5

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Resonant soft X-ray emission (RSXE) spectra of V_2O_3, VO_2 and NaV_2O_5 were recorded for a series of excitation energies at resonances of the V L- and O K-absorption band. The V L- and O K-emission in these vanadium oxide bands possess considerable overlap. By resonant excitation we can tune the energy to the absorption thresholds, thereby eliminating this overlap. Hereby we obtain the V 3d and O 2p projected density-of-states of the valence band. Resonant inelastic X-ray scattering (RIXS) is found to be weak in V_2O_3, which we explain as being due to its metallic character at room temperature. Vanadium dioxide (VO_2), semiconducting at room temperature, shows considerable RIXS features only at the O K-emission band. Distinct RIXS structures are visible in the RSXE spectra of the insulator NaV_2O_5. In the emission spectra excited at the V L-thresholds of this ternary vanadium oxide, dd-excitations of the V d_{xy} subband at an energy loss of -1.7 eV are observed. Our observation, that RIXS is stronger for insulators than for metals, should be taken advantage of for studying insulator-to-metal transitions in vanadium compounds in the future.

1. Introduction

3d transition metal oxides display a broad variety of electronic, magnetic and structural material properties. Vanadium oxides show different electronic behavior depending on their valence configuration. The binary vanadium oxides V_2O_3 [1–4] (with a formal valence shell configuration of V $3d^2$) and VO_2 [1–8] (formal configuration V $3d^1$) exhibit insulator-to-metal transitions at 160 K and 340 K, respectively.

The ternary vanadium oxide NaV_2O_5 (formal configuration V $3d^{0.5}$)[9] is particularly interesting because of its peculiar phase transition at 34 K, where it

is interesting to know whether charge ordering plays a role. The insulator NaV_2O_5 was considered to be the second example of an inorganic spin-Peierls (SP)[9,10] compound, showing many materials properties consistent with a SP transition at 34 K. More recent experimental data propose rather a charge ordering phase transition[11,12] at $T = 34$ K. In order to test the nature of the charge ordering phase transition in NaV_2O_5 model calculations of the electronic structure are generally compared with optical spectra.

The present work addresses the study of the electronic structure of these binary and ternary

vanadium oxides by means of soft X-ray absorption spectroscopy (SXAS) and resonant soft X-ray emission spectroscopy (RSXES). SXAS is employed to determine the resonant excitation energies for the RSXE spectra. RSXES is based on a two-photon process and maps the occupied valence electron states. Core electrons excited by X-ray photons undergo a transition to an intermediate core-excited state. This intermediate state decays to a final valence excited state or the ground state via fluorescence of an X-ray photon. In ordinary fluorescence, a relaxation step between the core-excited and the final state takes place, allowing the electronic system to dissipate energy. Moreover, with RSXES, low energy local electronic excitations can be studied due to resonant inelastic X-ray scattering (RIXS).[13] RIXS can be interpreted as an energy loss in RSXE spectra. It is not core-hole lifetime resolution limited and it is therefore capable of resolving such subtle features in the electronic structure as dd-excitations. By these means electron transitions in spectral ranges otherwise accessible only by optical absorption techniques can be studied without the restriction of selection rules for the allowed electron transitions.

In this work we investigated RSXE and RIXS structures of vanadium oxides in different oxidation states at room temperature. It is assumed that semiconductors or insulators should possess more pronounced RIXS contributions in the RSXE spectra than metals due to quenching of relaxation processes in the ordinary fluorescence.

2. Experimental

The investigated vanadium oxide samples were single crystals (approximately 2 mm × 2 mm × 0.1 mm). The experiments were performed at the undulator beam lines 7.0.1 at the Advanced Light Source (Lawrence Berkeley Laboratory) and at the bulk branch line of beam line I511 at MAX II (MAX-lab National Laboratory, Sweden). The X-ray absorption spectra were measured by recording the total electron yield (TEY) and the fluorescence yield (FY) while scanning the photon energy of the incident monochromatized synchrotron radiation. TEY absorption spectra were recorded by measuring sample drain current and FY absorption spectra were measured with a channel electron multiplier. The SXAS spectra were normalized to the photocurrent

from a clean gold mesh introduced into the synchrotron radiation beam in order to correct for intensity variations of the incident X-ray beam. The soft X-ray fluorescence was recorded with a high-resolution Rowland-mount grazing-incidence grating spectrometer[14] with a two-dimensional detector. The monochromator energy bandpass used for all SXAS spectra and for the excitation of the RSXES spectra was approximately 0.15 eV and 0.25 eV, respectively.

At beam line I511 (MAX II) refocusing optics situated in front of the measurement chamber and focusing the beam down to a vertical beam size of below 20 μm is employed. This facilitates taking RSXE spectra with opened slit of the soft X-ray emission spectrometer. By this high-resolution RSXE spectra can be recorded without losing much of the incident intensity of monochromatized X-ray photons. Usually a slit size of 10–20 μm has to be used in order to record high-resolution spectra.

3. Results and Discussion

Figure 1 displays the SXAS spectra of NaV_2O_5, VO_2 [1,4,7] and V_2O_3 [1,4] in TEY mode. All of these SXAS spectra are similar in the energy positions of the absorption bands. Between 512 eV and 528 eV the V L-spectra are split into the approximately 7-eV-separated spin–orbit doublet. The absorption band from 512–520 eV corresponds to the V $2p_{3/2} \rightarrow$
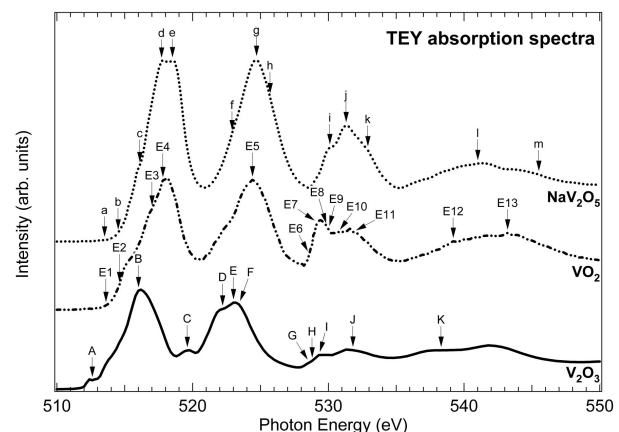

Fig. 1. V L and O K soft X-ray absorption spectra of NaV_2O_5, VO_2 and V_2O_3 in total electron yield mode. The excitation energies for the resonant soft X-ray emission spectra in Figs. 2–4 are marked by arrows above the spectra.

V 3d transition (V L_3) and the one from 520–528 eV to the V $2p_{1/2} \rightarrow$ V 3d transition (V L_2). Just above the V L_2-edge (528 eV) the O K-edge is found. The double-peaked part of the SXAS spectrum centered around 531 eV (528–534 eV) is attributed to O 2p states hybridized with unoccupied crystal field split V 3d states. The structure around 542 eV is interpreted according to a hybridization of O 2p states with V 4sp states. Note that the absorption spectra taken in TEY and FY mode behave similarly, apart from a reduced intensity of the V L-bands in the FY mode spectrum (not shown here) relative to the O K-band. Therefore it was reasonable to choose the proper excitation energies for the RSXES from the TEY spectrum, being recorded with higher statistics.

Figure 2 shows the RSXE spectra excited at the energies indicated by the arrows in the V_2O_3 SXAS

spectrum in Fig. 1. The V L_α-band (3d4s $\rightarrow 2p_{3/2}$) and the V L_β-band (3d4s $\rightarrow 2p_{1/2}$) are centered at 512 eV and 519 eV, respectively, and have considerable overlap. Above the V L-emission band region (see the bar markings on the energy scale of Fig. 2) the O K_α-emission band is spread around 524 eV. The overlap of the V L_β-band with the O K_α-band is again visualized with marked energy regions on the energy scale of the emission spectra.

By resonant excitation we can tune the energy to the V $2p_{3/2}$ threshold, thereby eliminating this overlap. Thus the bottom spectrum A of Fig. 2 can be considered as the V 3d projected density-of-states (DOS) of V_2O_3. The top three spectra are dominated by the O K_α-emission. Here the O 2p character of the valence band is reflected. Figure 3 compares RSXE spectra (A and I in Fig. 2) excited at the V $2p_{3/2}$ and the O 1s threshold, respectively. In this comparison both spectra are aligned relative to the assumed position of the Fermi edges. Using this
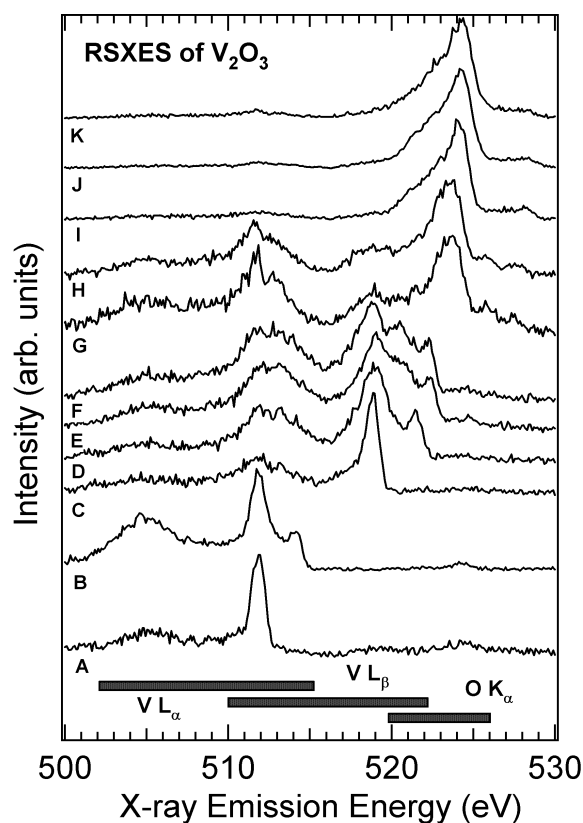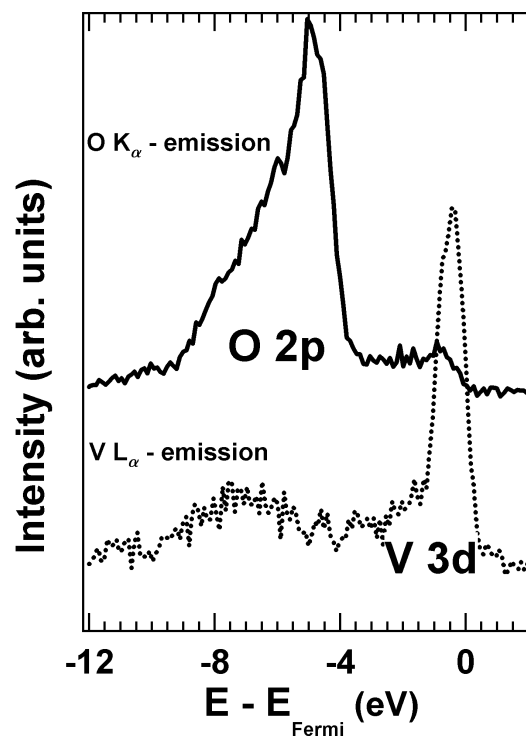

Fig. 2. Resonant soft X-ray emission spectra of V_2O_3 excited at the energies indicated by the arrows A–K in the corresponding absorption spectrum in Fig. 1. The energy regions of the overlapping V L_α-, V L_β- and O K_α-emission bands are marked with bars on the energy scale.

Fig. 3. Comparison of O K_α- (full line) and V L_α-emission spectra (dotted line) of V_2O_3. The spectra are aligned relative to the assumed position of the Fermi energy. Both emission spectra consist of O 2p and V 3d components and visualize the strong hybridization between the O 2p and V 3d bands in V_2O_3.

convention the energy scale used corresponds to a negative binding energy. Obviously, in V_2O_3 the O 2p and V 3d bands are strongly hybridized with each other, since both spectra consist of O 2p and V 3d components.

Resonant inelastic X-ray scattering (RIXS) is weak compared to ordinary fluorescence features, which is probably due to the metallic character of V_2O_3 at room temperature. Nevertheless, in spectra D–H we see energy loss features which we attribute to dd-excitations in the V 3d band. These low energy excitations overlap with the high energy side of the V L_β- and O K_α-emission band, respectively. In Fig. 4 spectra D–I are plotted as RIXS spectra against an energy loss scale relative to the elastic peaks of the RSXE spectra in Fig. 2. Here the RIXS peak is found at a constant energy loss of approx. -1.7 eV. In the RIXS spectrum D the inelastic scattering structure overlaps with the ordinary V L_β-fluorescence and can just be seen as a shoulder. Spectrum I was considered as pure O K_α-emission in the discussion above. Here the inelastic contributions are very weak.

Fig. 5. Resonant soft X-ray emission spectra of VO_2 excited at the energies indicated by the arrows E1–E13 in the corresponding absorption spectrum in Fig. 1.
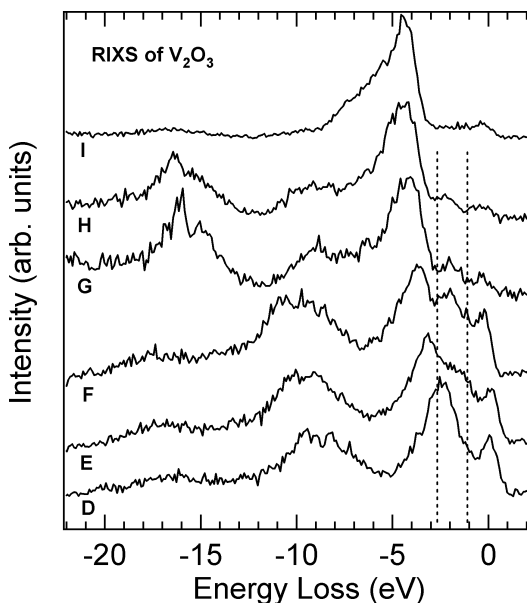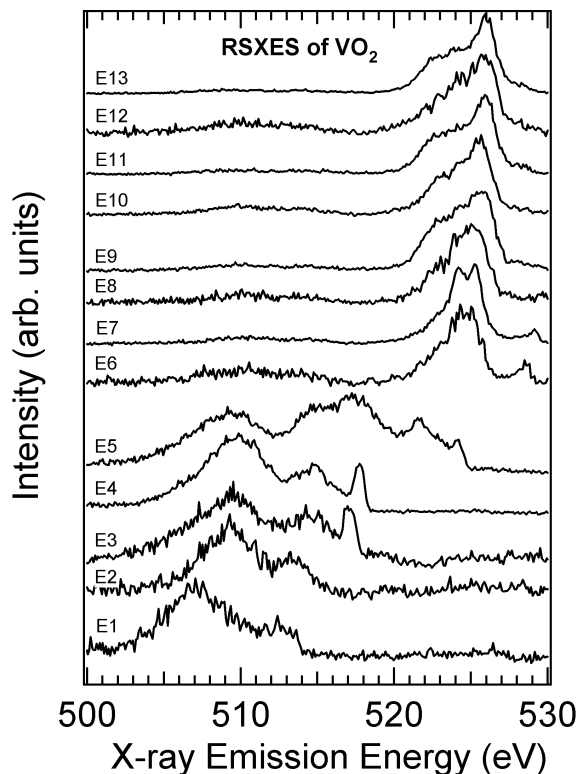
Fig. 4. Resonant inelastic X-ray scattering spectra of V_2O_3 excited at V L- and O K-edge energies, indicated by the arrows D–I in the corresponding absorption spectrum in Fig. 1. The spectra are plotted against an energy loss scale relative to the elastic peaks in the resonant soft X-ray spectra of Fig. 2. An inelastic feature situated around an energy loss of -1.7 eV, which is probably corresponding to a dd-excitation, is marked through dashed lines in the figure.

The RSXE spectra of VO_2 excited at the resonant energies indicated by the arrows E1–E13 in the corresponding SXAS spectrum (cf. Fig. 1) are displayed in Fig. 5. Again the O 2p and V 3d bands are strongly hybridized. In spectrum E4 the band around 510 eV can be considered as the O 2p derived DOS. The V 3d-derived DOS can be seen around 515 eV in this spectrum. The energy dependence of the O K_α-emission band is thought to be due to RIXS features and excitation of different oxygen sites in the soft X-ray emission. Although spectra E1–E3, excited at the V $2p_{3/2}$ threshold, also show considerable spectral changes (RIXS), it is less obvious to assign a clear energy position to for example, dd-excitations, which is another indication for the lower degree of correlation of this compound.[6] Furthermore, we do not observe any structures at an energy loss of -6 eV which Shin *et al.*[5] previously had observed and interpreted as a charge transfer excitation.

Figure 6 displays the RSXE spectra of NaV_2O_5 at the excitation energies assigned by the arrows
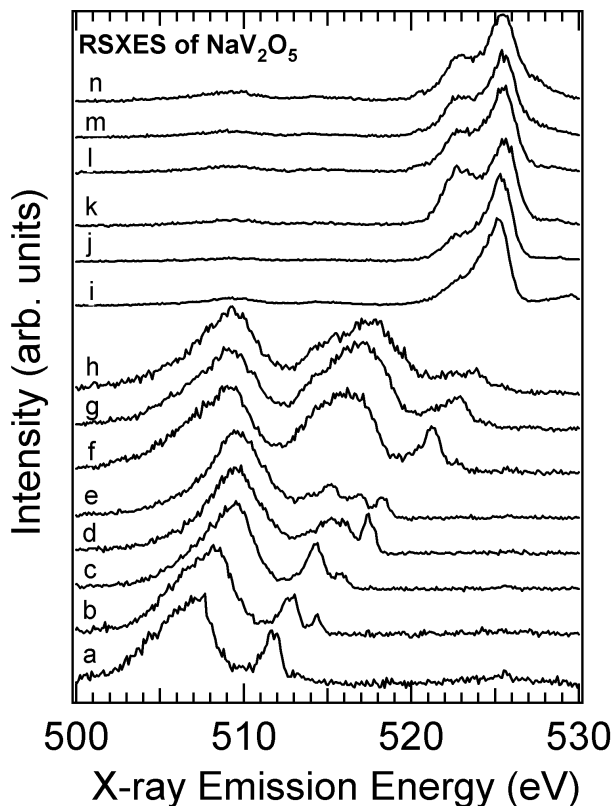
Fig. 6.   Resonant soft X-ray emission spectra of NaV_2O_5 excited at the energies indicated by the arrows a–n in the corresponding absorption spectrum in Fig. 1.
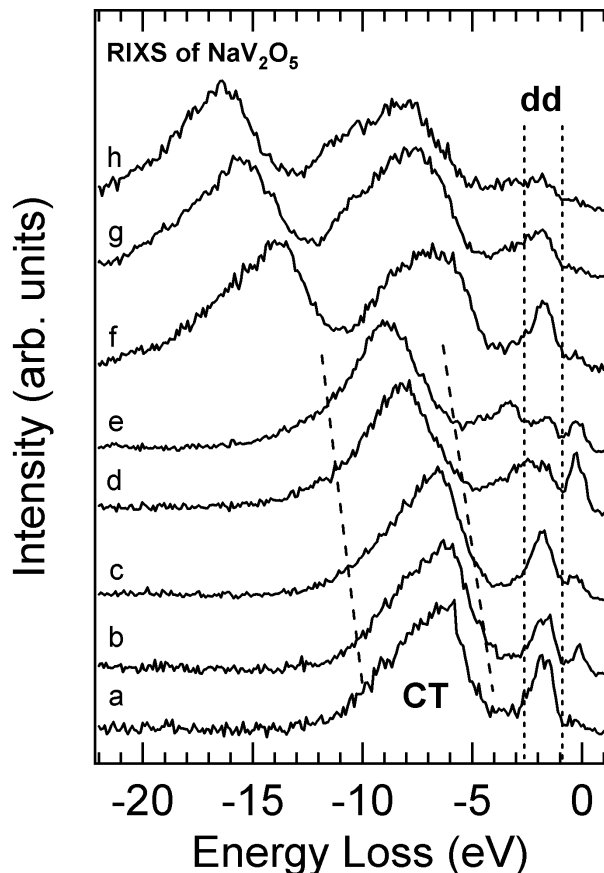

Fig. 7.   Resonant inelastic X-ray scattering spectra of NaV_2O_5 excited at V L-edge energies indicated by the arrows a–h in the corresponding absorption spectrum in Fig. 1. The spectra are plotted against an energy loss scale relative to the elastic peaks in the resonant soft X-ray emission spectra of Fig. 6. A peak at an energy loss of approx. -1.7 eV corresponding to a dd-excitation and a band of charge transfer states around -6.5 eV are marked through dashed lines.

(a–n) in the corresponding SXAS spectra in Fig. 1. A prominent feature in the resonantly excited spectra (a–h) at the V L thresholds disperses linearly with the elastic peak at an energy distance of approximately 1.7 eV. This inelastic loss structure is therefore most likely due to a dd-excitation in the crystal field split 3d multiplets. Therefore the band around 508 eV in X-ray emission energy cannot be interpreted as just ordinary V L-emission. Instead we interpret this as charge transfer (CT) states ($V3d^2$ $\underline{L}$) showing up as RIXS features in our spectra. Spectra i–n show the O K_α-emission spectra and display mainly the O 2p-projected DOS. Here RIXS seems to be less prominent than in the V L-emission spectra. In Fig. 7 the RSXE spectra a–h are plotted against an energy loss scale relative to the elastic peaks. This visualizes the presence of a dd-excitation peak at a constant energy loss of -1.7 eV.

In spectra a–c of Fig. 7 a band situated around an energy loss of -6.5 eV originating from CT states

can be seen. Beginning with spectrum d, which is excited at the maximum of the V L_3 absorption band, the CT band overlaps with the ordinary V L_α-emission. In the same spectrum a peak at lower energy next to the dd-excitation peak occurs and is considered as the beginning of the normal V L_β-emission. Spectra a–c are thought to be consisting only of RIXS contributions.

Previously suggested dd-excitations at energies of 0.9–1.0 eV [11,12] and 1.25 eV [10] are not present in our investigations of NaV_2O_5. This may support the alternative interpretation of the authors of Refs. 11 and 12, where the spectral feature seen in optical

conductivity data at around 0.9–1.0 eV is attributed to a bonding–antibonding transition within the V–O–V rung. The peak seen in optical absorption at 1.25 eV [10] cannot, following our investigations, be attributed to a dd-excitation. However, we have clear evidence for a dd-excitation at an energy loss of -1.7 eV in the V L-RIXS spectra and a charge transfer excitation at an energy loss of -6.5 eV. Theoretical calculations using a V $3d^1$-configuration lead to the same salient RIXS features. Further model calculations for the $3d^{0.5}$-configuration are in preparation.[15]

4. Conclusions

The V L- and O K-emission bands in RSXE spectra of the present vanadium oxides (V_2O_3, VO_2 and NaV_2O_5) possess considerable overlap. In these vanadium compounds RSXE spectra at the absorption thresholds can be excited and thereby the V 3d and O 2p projected density-of-states of the valence band can be obtained. V L- and O K-emission spectra consist both of components originating from O 2p and V 3d bands for these three materials. This visualizes the strong hybridization between O 2p and V 3d electrons in all of them. RIXS is found to be weak in V_2O_3, which is explained by its metallic character at room temperature. Nevertheless, a faint dd-excitation peak at an energy loss of approx. -1.7 eV is found for V_2O_3. Vanadium dioxide (VO_2), semiconducting at room temperature, shows considerable RIXS features at the O K-emission band. In the emission spectra excited at the V L-thresholds of the charge transfer insulator NaV_2O_5, dd-excitations of the V d_{xy} subband at an energy loss of -1.7 eV are observed together with charge transfer excitations around -6.5 eV in photon energy loss. Our observation that dd-excitations observed by RIXS seem stronger for insulators than for metals should be utilized for studying insulator-to-metal transitions in vanadium compounds in the future. However, as can be seen from the example of VO_2, it is not sufficient to have an insulating state for obtaining a strong contribution of dd-excitations in RIXS. Rather, the degree of electron correlation and localization is most likely a key factor. That has to be taken into account when investigating RIXS spectra below and above the transition temperatures for metal-to-insulator transitions.

References

1. R. Zimmermann *et al.*, *J. Phys.: Condens. Matter* **10**, 5697 (1998).
2. F. Werfel, G. Dräger and U. Berg, *Cryst. Res. Tech.* **16**, 119 (1981).
3. S. Shin *et al.*, *Phys. Rev.* **B41**, 4993 (1990), and references therein.
4. L.-C. Duda *et al.*, in Materials Research Society Symposium Proc. Vl. 494, *Science and Technology of Magnetic Oxides*.
5. S. Shin *et al.*, *J. Electron Spectros.* **79**, 125 (1996).
6. E. Z. Kurmaev *et al.*, *J. Phys.: Condens. Matter* **10**, 4081 (1998).
7. M. Abbate *et al.*, *Phys. Rev.* **B43**, 7263 (1991).
8. P. B. Allen *et al.*, *Phys. Rev.* **B48**, 4359 (1993).
9. M. Lohmann *et al.*, *Phys. Rev. Lett.* **85**, 1742 (2000).
10. S. A. Golubchik *et al.*, *J. Phys. Soc. Jpn.* **66**, 4042 (1997).
11. C. Presura *et al.*, *Phys. Rev.* **B62**, 16522 (2000).
12. M. J. Konstantinovic *et al.*, *Phys. Rev.* **B63**, 121102 (R) (2001).
13. S. M. Butorin *et al.*, *Phys. Rev.* **B54**, 4405 (1996); S. M. Butorin *et al.*, *Phys. Rev.* **B55**, 4242 (1997); A. Kotani and S. Shin, *Rev. Mod. Phys.* **73**, 203 (2001).
14. J. Nordgren *et al.*, *Rev. Sci. Instrum.* **66**, 1690 (1989).
15. T. Schmitt *et al.*, in preparation.